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# Fuel-Rich Catalytic Combustion

*A Soot-Free Technique for  
In Situ Hydrogen-Like  
Enrichment*

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National Aeronautics  
and Space Administration

Scientific and Technical  
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## Summary

An experimental program on the catalytic oxidation of iso-octane demonstrated the feasibility of a two-stage combustion system for reducing particulate emissions. With a fuel-rich ( $\phi = 4.8$  to 7.8) catalytic combustion preburner as the first stage the combustion process was soot free at reactor outlet temperatures of 1200 K or less. Although soot was not measured directly, three pieces of data indicated its absence: (1) measured reactor outlet temperatures followed closely those calculated by an equilibrium program when carbon was omitted as a product, (2) the hot reaction products were completely transparent and emitted none of the radiation associated with carbon, and (3) a good carbon-atom balance across the reactor was calculated from the measured reaction products.

Reaction products collected at two positions downstream of the catalyst bed were analyzed on a gas chromatograph. Comparison of these products indicated that pyrolysis of the larger molecules continued along the drift tube and that benzene formation was a gas phase reaction.

The effective hydrogen-carbon ratio calculated from the reaction products increased by 20 to 68 percent over the range of equivalence ratios tested. Such an increase in a poor fuel could produce an excellent fuel. The catalytic partial oxidation process also yielded a large number of smaller carbon-containing molecules. The percentage of fuel carbon in compounds having two or fewer carbon atoms ranged from 30 at 1100 K to 80 at 1200 K.

## Introduction

The soot produced in practical combustion systems has become a problem because of its effect on combustor life and because it fails to meet environmental standards. This problem is expected to get worse as the quality of fuel deteriorates. The amount of soot formed in a gas turbine combustor scales approximately as the ratio of the hydrogen to carbon in the fuel (i.e., the smaller this ratio, the more soot produced). The ratio can be altered either at the refinery or in the combustion process. Clayton (ref. 1) presents a concept for changing this ratio by adding large amounts of hydrogen to the fuel in the

combustion chamber. Izquierdo and Hoult (ref. 2) altered the ratio by using methanol as a fuel additive in the combustion chamber. The concept presented in the present report is a staged combustion process that increases the hydrogen-carbon ratio of the fuel by removing some of the carbon atoms from the soot-forming process. This is done by partial oxidation reactions that form carbon-oxygen bonds.

This work was prompted by the research of Street and Thomas (ref. 3), who studied the formation of carbon in premixed flames for several classes of organic compounds, some of which contained oxygen atoms. They conclude that when a carbon atom is connected to an oxygen atom, the carbon atom cannot participate in the soot-forming process. A good example of this can be seen in the results of methane and methanol combustion. Even though both species have the same hydrogen-carbon ratio, methane can easily be made to smoke, but methanol, whose only carbon atom is bonded to an oxygen atom, cannot be made to smoke under any conditions.

This effect can also be seen in the data of Clarke, Hunter, and Garner (ref. 4), who studied the smoking tendency of several classes of organic compounds. The smoke point of several straight-chain organic compounds versus the number of carbon atoms in the molecule is plotted in figure 1. The smoke point is defined as the height in millimeters of the highest flame produced without smoking when the fuel was burned in a specific test lamp. Although the oxygen-containing compounds all have higher smoke points than the corresponding hydrocarbons, no direct correlation can be obtained from the data. However, if all of the carbon atoms connected to oxygen atoms are removed as soot-forming candidates, as suggested by Street and Thomas, the data collapse into a single curve (fig. 2). It seems clear that the conclusion of Street and Thomas is correct and has a great deal of merit.

Partial oxidation of a hydrocarbon fuel to form oxygen-containing compounds is a fuel-rich combustion process that usually forms soot, an undesirable product. A technique for avoiding the formation of soot was suggested by one of Street and Thomas' observations. They observed that carbon did not form in very rich flames near the upper limit of flammability. Burgoyne and Neal (ref. 5) also observed this effect and suggested

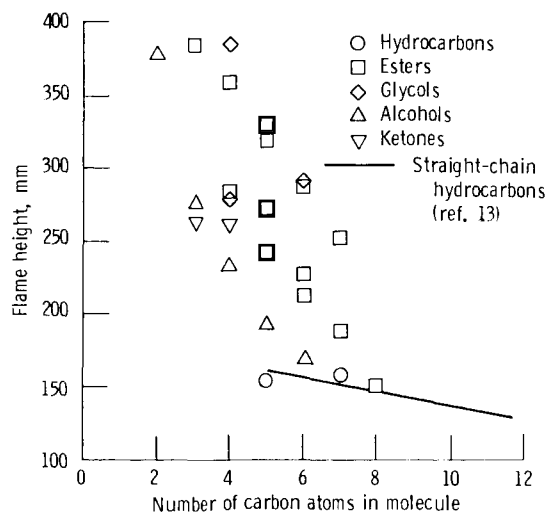


Figure 1.—Smoke points of various types of straight-chain organic compounds versus number of carbon atoms in molecule.

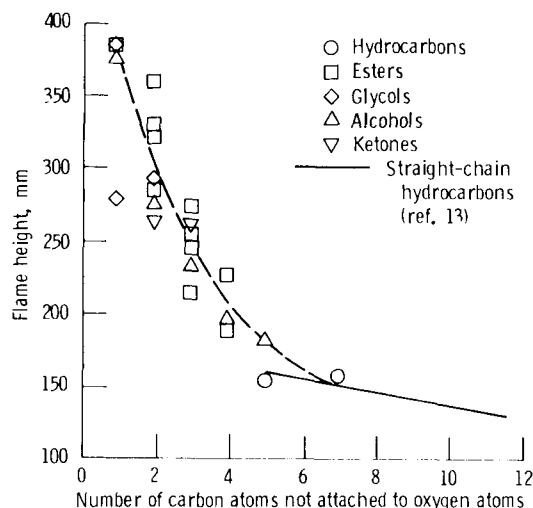


Figure 2.—Smoke points of compounds in fig. 1 with carbon atoms connected to oxygen atoms subtracted from total carbon atoms in each molecule.

that very rich flames may be too cool for carbon to form. Since the temperature of the rich limit of combustion for most hydrocarbons is 1200 to 1300 K, the shock tube experiments of Graham et al. (ref. 6) support this suggestion. In studying the pyrolysis of various hydrocarbon fuels, they found that soot was not formed in any measurable amounts until the temperature was near 1500 K, well above the temperature of the rich limit.

It was concluded that partial oxidation of a fuel could change the effective hydrogen-carbon ratio of the resulting products and produce a cleaner-burning fuel. In contrast to the usual fuel-rich combustion, which does form soot, partial oxidation of a fuel can be accomplished soot free by burning at equivalence ratios near or beyond the rich limit of combustion. Therefore catalytic oxidation of iso-octane at equivalence ratios from 4.8 to

7.8 was studied at an air inlet temperature of 800 K. The objectives of this research were to demonstrate the feasibility of soot-free, fuel-rich catalytic oxidation as a viable approach to in situ hydrogen-like enrichment of a fuel.

## Experimental Apparatus and Procedures

The experimental apparatus consisted of a catalytic flow-tube reactor (fig. 3) made of two concentric tubes approximately 2.5 m long, with an inner diameter of 5 cm and an outer diameter of 11.4 cm. Although the thin-walled stainless steel inner tube was surrounded by 3.2 cm of insulation, additional external insulation was required from the air heater to the catalyst bed. Ports were available along the length of the reactor for mounting thermocouple probes, pressure probes, and the sampling probe. Two calcium fluoride windows were placed opposite each other 7.6 cm downstream of the catalyst bed so that visual or optical observations could be made of the combustion gases.

### Fuel Injector

The design of the fuel injector was based on the work of Tacina (ref. 7). The seven 10-cm-long conical nozzles were arranged with six in a circle and one in the center. The inlet diameter of each cone was 0.50 cm and the outlet diameter was 1.37 cm. Fuel was delivered to each cone through lines of equal length that were bent to spray the fuel in the direction of the airflow. Downstream temperature measurements indicated that this gave good fuel distribution for equivalence ratios below about 8.0.

### Catalyst Bed

The catalyst bed was made with an expanded inner diameter of 7.2 cm so that the monoliths could be held in a permanent position (fig. 4). Examination of the used catalyst showed this to be a poor method for restraining the monoliths since pyrolyzed fuel was found around the outer edges of the monolith in the stagnant zone outside the main flow stream. However, this carbon buildup probably occurred during the long warmup, and the carbon-atom balance indicated that it had no effect on the present data. The catalyst used in these experiments was a 2:1 mixture by weight of palladium/platinum applied to cordierite honeycomb substrates coated with an alumina washcoat.

The substrates were 2.54 cm thick and had cell densities of 4 to 31 square cells/cm<sup>2</sup>. The total metal loading of the catalyst was 1.482 kg/m<sup>3</sup>. To assign a numerical value to the amount of catalyst being used, external surface areas were calculated for each size monolith. The values are shown in figure 4 along with the catalyst configuration used.

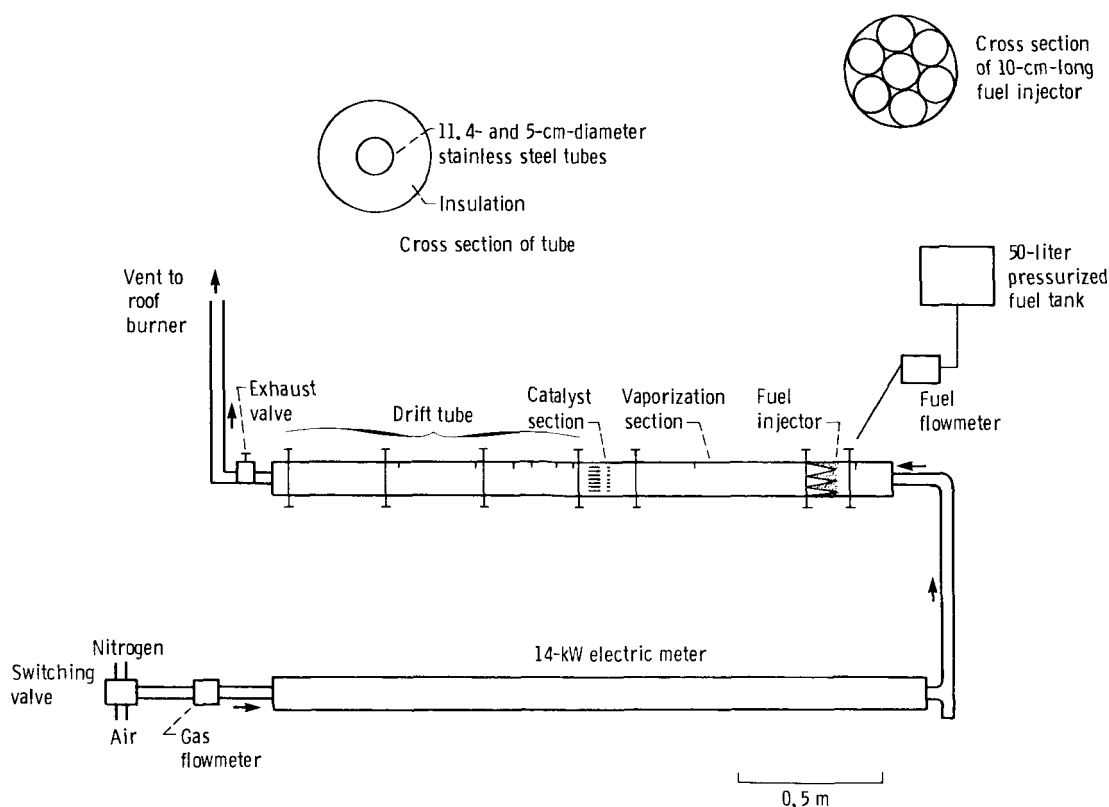


Figure 3.—Schematic drawing of catalytic flow tube reactor.

Monolith	Cell density, cm <sup>2</sup>	Surface area, cm <sup>2</sup>
1	31	768
2	15.5	522
3	7.75	334
4	3.88	275

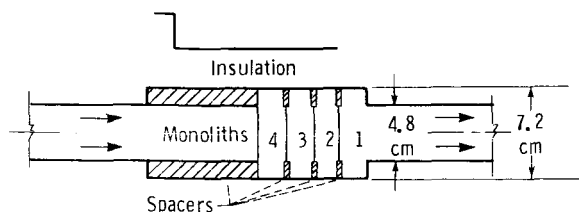


Figure 4.—Description of catalyst, configuration, and holder.

reaction products. This venting caused the gas velocity to increase by about a factor of 3 across the 10 cm of the catalyst bed.

Standard procedures were followed for each run. These included a warmup of at least 90 min with hot nitrogen followed by an additional warmup of 30 to 50 min at the desired test conditions. This procedure produced steady-state temperatures in the reactor. The flow system was designed to permit switching the gas from nitrogen to air without interrupting the flow. Thus the fuel flow rate was established with hot nitrogen before switching to hot air. This ensured that the equivalence ratio in the reactor was always rich and that the catalyst never experienced a stoichiometric condition.

## Operating Procedures

Airflow through the reactor was controlled by setting the supply pressure and varying the opening of the exhaust valve at the end of the reactor. A calibrated strain gauge flowmeter measured the airflow, which was kept constant at about 0.4 std m<sup>3</sup>/min. The pressure at the inlet to the catalyst bed was maintained at about 200 kPa. The addition of fuel and the subsequent chemical reaction required further adjustment of the exhaust valve to accommodate the larger gas volume produced by the changes in temperature and in the number of moles of

## Fuel

Iso-octane was used because it is easily and inexpensively obtained in large quantities with high purity. Analyzing the oxidation products of a single compound was expected to be simpler than analyzing a mixture like kerosene or jet fuel. A liquid fuel was used because it was important to simulate a practical fuel. Fuel was pressure fed to the reactor through a metering valve, and the flow rate was measured with a calibrated turbine flowmeter. Flow rates varied from 200 to 350 cm<sup>3</sup>/min, depending on the equivalence ratio desired.

## Sampling and Analysis of Product Gases

Samples were withdrawn from the reactor in two locations, 17.8 and 67.3 cm downstream of the catalyst bed, corresponding to 15.9 to 19.5 msec and 59.6 to 64.2 msec of gas-phase reaction time (dwell time). The sampling probe was a 0.33-cm-diameter stainless steel tube with three 0.06-cm-diameter holes spaced 1.3 cm apart. The three holes were positioned in the center 2.5 cm of the reactor diameter. Samples were withdrawn through lines heated to about 375 K into an ice bath condenser, where the liquids were trapped. The gas continued through a metal bellows type of sampling pump to a 1-liter stainless steel sampling bottle. The bottle was pressurized to about 200 kPa. A wet test meter measured the sampling rate. At the end of a sampling run liquids were collected and the volume per liter of reaction gas was determined. A grease, which solidified on the sides of the condenser tube, was dissolved in acetone and stored. The combustion products were analyzed on a gas chromatograph with a thermal conductivity detector. Ultra-high-purity helium was used as the carrier gas. A computing integrator determined peak areas from the detector signal. Three columns were used in analyzing the reaction product gases: washed molecular sieve, Spherocarb, and Porapak S. The external-standard method was used to determine concentrations of the species in the sample. This method compares the integrated area of a standard mixture to the area of the sample.

Except for hydrogen, concentrations were reproduced to better than 1 percent for all of the light gases ( $O_2$ ,  $N_2$ ,  $CO$ ,  $CO_2$ ,  $C_2H_6$ ,  $C_2H_4$ , and  $C_2H_2$ ). Hydrogen, because its thermal conductivity is similar to that of the helium carrier gas, was difficult for the detector to "see." The reproducibility of the hydrogen concentration was only about 2 percent. Some of the heavier hydrocarbons' concentrations were difficult to reproduce because they were so small. Toluene was the worst case with only 3 percent reproducibility. Table I lists the reaction products found with concentrations greater than 0.03 percent.

## Condensates in Cold Trap

In addition to gaseous products, condensable reaction products were also collected. The condensate contained both a liquid and a grease-like solid. The liquid collected for 45 liters of gas was used to determine the density, pH, and volume of liquid per liter of gas. These numbers are recorded in table I. It appears that the liquid is mostly water with small amounts of an acid. The grease removed from the inside of the condenser has not been identified. The grease was soluble in acetone and had reasonable vapor pressure. Although the liquid measurements were crude, they were useful in producing reasonable oxygen and hydrogen balances across the catalyst bed. Assuming

the liquid was water, the products accounted for 96 percent of the reactant hydrogen and 98 percent of the oxygen.

## Carbon on Catalyst

Run times for a given test were a little over an hour, and 12 to 21 liters of fuel was processed. Early testing indicated that some carbon was formed on the surface of the catalyst. To ensure that the nature of the catalyst was not changed from run to run, this small amount of carbon was removed by purging the system with hot air after each test. The purge was completed in 1 to 2 min, and the temperature during the purge rose less than 50 deg K. Considering the amount of fuel processed, the amount of carbon formed was insignificant.

## Results and Discussion

### Temperature Profiles Upstream of Catalyst

Gases must be well mixed and distributed before reaching the catalyst bed as mixing does not occur between monolith channels. To determine the extent of vaporization and mixing upstream of the catalyst, temperature profiles were taken across the diameter of the reactor. Temperatures were measured with an iron-constantan open thermocouple positioned at various locations across the reactor 10 cm upstream of the bed. Temperature profiles of the flow are shown in figure 5 for equivalence ratios of 5.35 to 7.55. The temperature across the reaction zone varied by about 3 deg K at  $\phi = 5.35$  and by 11 deg K at  $\phi = 7.55$ . The change from a symmetric profile at  $\phi = 5.35$  to an unsymmetric one at  $\phi = 7.55$  indicated that more fuel was at the bottom of the tube than at the top and limited the usable upper equivalence ratio to something less than 8.0.

Centerline temperatures of the fuel-air mixture are plotted in figure 6 as a function of equivalence ratio and compared with the calculated temperatures (solid line) for inlet air at 800 K and liquid iso-octane at 298 K. The experimental data, corrected to these conditions, are in good agreement with the theoretical line.

### Temperature Profiles Downstream of Catalyst

The reaction temperature profiles (fig. 7) were measured 3.8 cm downstream of the bed with a standard 0.16-cm-diameter closed thermocouple probe. A closed couple was required in this region because fuel absorbed by the insulation around the wires pyrolyzed and the carbon buildup in the insulation caused the resistance of the probe to drop from over a megohm to a few hundred ohms. The temperature in the sampling zone varied by about 5 deg K and showed little change as the equivalence ratios changed. The flat profile at the higher equivalence

TABLE I.—REACTION PRODUCTS

	Position 1 (17.8 cm downstream)					Position 2 (67.3 cm downstream)			
Reaction temperature, K	1200	1170	1138	1114	1093	1213	1198	1181	1145
Equivalence ratio	4.80	5.50	6.56	7.22	7.87	4.82	5.11	5.51	6.26
Fuel flow, moles/min	1.266	1.465	1.751	1.937	2.099	1.265	1.359	1.468	1.666
Airflow, moles/min	15.75	15.89	15.93	16.00	15.92	15.66	15.86	15.90	15.86
Dwell time, msec	15.9	16.1	17.3	18.5	19.5	59.6	60.3	60.9	64.2
Catalyst bed pressure, kPa									
Upstream pressure	198.4	197.4	197.3	198.5	198.6	198.9	199.7	197.3	197.6
Downstream pressure	196.7	197.4	196.7	197.6	197.8	197.8	198.4	196.8	197.3
$\Delta P$ across bed	1.7	0	.6	.9	.8	1.1	1.3	.5	.3
Reactor temperature, K									
Preheated air	815	813	814	813	811	820	818	815	811
Vaporization	549	532	508	491	476	551	543	533	513
Gas sample concentrations, vol % of dry gas									
Group 1:									
Hydrogen	12.54	12.11	8.28	5.84	4.58	10.93	10.30	9.46	7.9
Oxygen	.73	.75	.79	.87	.92	.65	.63	.66	.69
Nitrogen	53.23	53.10	55.86	58.14	59.93	52.69	53.18	53.76	54.66
Carbon monoxide	17.41	16.32	13.28	11.49	10.33	17.43	16.64	15.47	14.58
Carbon dioxide	1.78	2.07	2.68	3.10	3.37	1.53	1.83	2.20	2.70
Methane	6.34	5.83	6.12	5.71	4.91	8.86	8.82	8.79	8.16
Acetylene	.15	.08	.06	.03	.04	.61	.40	.30	.14
Ethylene	4.08	3.21	4.20	3.29	2.00	4.62	4.85	4.65	4.43
Ethane	.42	.50	.59	.51	.48	.21	.29	.42	.55
Total	96.68	93.97	91.86	89.00	86.56	97.53	96.94	95.71	93.81
Group 2:									
Propylene	1.66	2.57	3.61	4.13	4.13	0.62	1.13	1.52	2.76
Allene	.24	.25	.22	.16	.13	.12	.16	.20	.29
Methyl acetylene	.20	.16	.12	.10	.10	.23	.26	.29	.26
C <sub>4</sub> hydrocarbons	1.42	2.77	4.05	5.59	6.17	.54	.26	.94	2.54
C <sub>5</sub> hydrocarbons	.06	.23	.48	.91	.95	.06	.04	.11	.31
Benzene	.12	.09	.10	.09	.09	.36	.39	.43	.35
Toluene	.03	.03	.04	.21	0	.07	.08	.11	.13
Iso-octane	0	.03	.24	.89	2.04	0	0	0	0
Total of groups 1 and 2	100.42	100.10	100.74	101.26	100.26	99.53	99.26	99.32	100.47
Liquid sample data									
Liquid deposit, cm <sup>3</sup> /liter	0.033	0.028	0.061	0.059	0.073	0.024	0.033	0.028	0.043
Density, g/cm <sup>3</sup>	1.00	1.05	1.01	1.05	1.03	1.01	1.02	1.00	1.02
pH	4.5	4.5-5	4.5-5	4-4.5	4-4.5	4.5	4.0	6.0	6.0

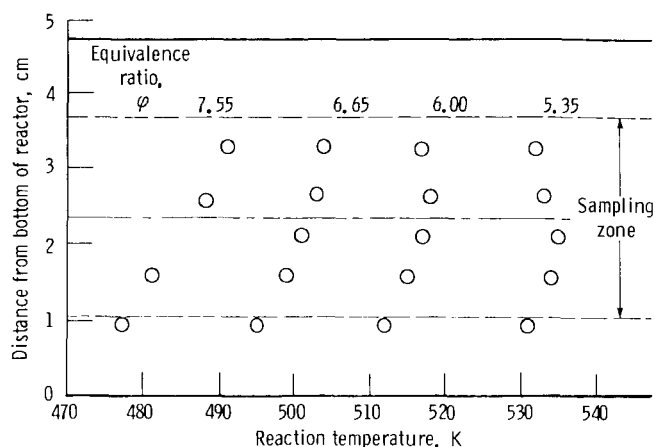


Figure 5.—Reaction temperature profiles of vaporized fuel-nitrogen mixtures upstream of catalyst bed for several equivalence ratios.

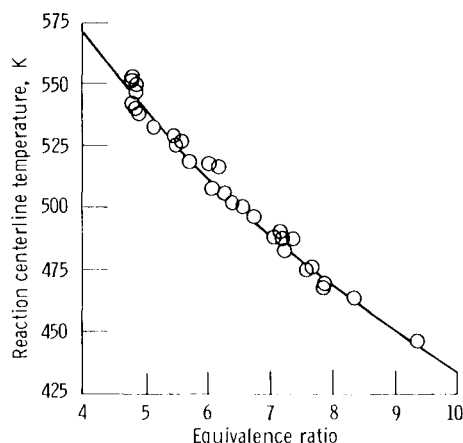


Figure 6.—Comparison of measured vaporization temperature with theoretical temperature versus equivalence ratio.

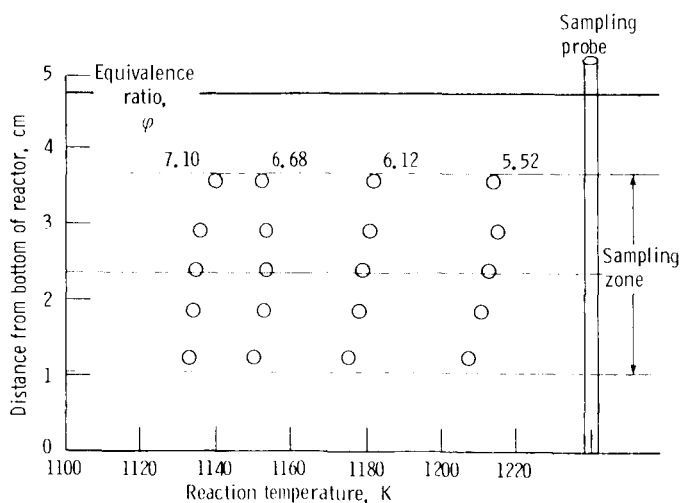


Figure 7.—Reaction temperature profiles 3.8 cm downstream of catalyst for several equivalence ratios.

ratios, where vaporization profiles were skewed, suggests that some mixing may have occurred between catalyst monoliths.

### Reaction Products

Gas samples were withdrawn at two locations downstream of the catalyst. The first location (17.8 cm) yielded the products resulting from both surface and gas-phase reactions; the second location (67.3 cm) showed the effect of a much longer gas-phase dwell time. Table I shows a side-by-side comparison of the reaction products, temperature, equivalence ratio, and dwell time for samples withdrawn at the two locations. The reaction products have been divided into two groups to show the fuel-processing character of the preburner. Group 1 contains  $H_2$ ,  $O_2$ ,  $N_2$ , and all  $C_1$  and  $C_2$  carbon-containing compounds, while group 2 contains  $C_3$  to  $C_8$  compounds. As the equivalence ratio increased, percentages of some products increased, some decreased, and others stayed the same. Carbon monoxide, methane, hydrogen, acetylene, and ethylene decreased; carbon dioxide, water, propylene, and  $C_4$  and  $C_5$  compounds increased. Ethane, benzene, and toluene showed little change.

Figure 8 presents the volume percentages of some of the products as a function of measured reaction temperature for two dwell times. The lines are eyeball fits to the data and were meant to demonstrate that the trends at the two dwell times are similar even though the volume percentages are different. Comparing the products at the two dwell times indicates that gas-phase reactions continued along the drift tube. Propylene,  $C_4$  hydrocarbons, iso-octane, and hydrogen volume percentages decreased; methane, ethylene, and benzene increased. Apparently pyrolysis reactions involving the larger compounds and hydrogen produced the smaller compounds and benzene. Benzene is interesting in that its volume percentage depends not on the temperature or equivalence ratio but rather on the length of time available for the products to react (fig. 9). Assuming that at zero time the benzene content is zero, a reasonably straight line can be drawn through the data points. This may suggest that benzene is formed in the gas phase from the compounds found in the analysis at a rate of about  $10^{-6}$  mole/cm<sup>3</sup> sec.

### Inspection of Reactor for Carbon Deposits

After 840 min of testing the catalyst was removed and the reactor inspected for carbon deposits. During this period of testing about 250 liters of fuel had been processed. Pyrolyzed fuel was found in the stagnant region outside the main flow stream. However, the catalyst itself showed no trace of carbon deposits in any of the channels where flow had been maintained. In the



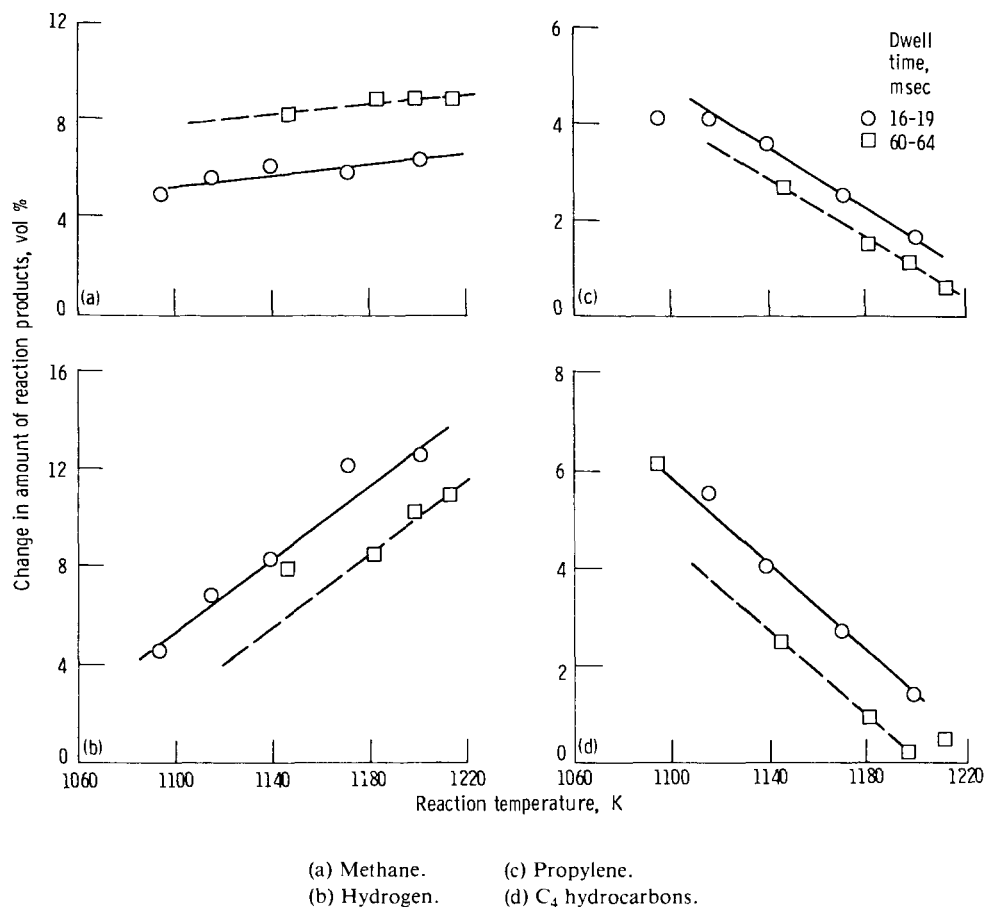


Figure 8.—Change in percentage of reaction products versus temperature and dwell time.

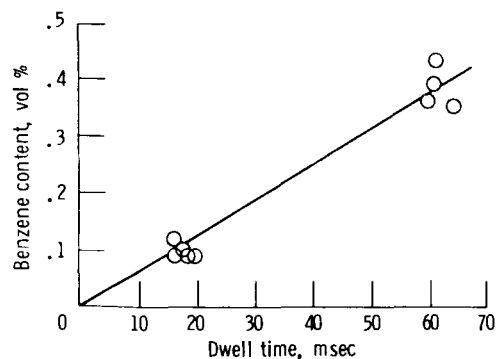


Figure 9.—Benzene content versus dwell time.

drift tube downstream of the catalyst bed, some black deposits were found on the walls and the sampling probe. These deposits were loose and flaked off easily. They were not the flocculent deposits characteristic of sooting flames. One possible source of this carbon may have been the pyrolysis of the grease-like substance found in the cold trap during sampling. Considering the volume of fuel processed, the amount of carbon was insignificant.

### Reaction Temperatures

The reaction temperature was measured 3.8 cm downstream of the catalyst bed. This temperature is a function of the equivalence ratio and the temperature of the preheated gas. Because platinum/palladium catalyst is deactivated rapidly at temperatures near 1300 K, the

maximum outlet temperature was limited to about 1200 K. This corresponds to a preheat temperature of 800 K and an equivalence ratio of about 4.8. This ratio can be varied by increasing or decreasing the preheat temperature of the air.

The measured reaction temperatures were compared with reaction temperatures calculated by assuming that soot was or was not a product (fig. 10). The equilibrium calculations were performed with the Lewis equilibrium program (ref. 8), which contains thermodynamic data for about 135 C-H-O-N species. This large data base was important because the no-soot calculated reaction temperatures depend not only on the initial conditions of the reactants (equivalence ratio and temperature), but also on which species were considered to be reaction products. The temperature for the two calculations differed by about 150 deg K, and as can be seen, the measured reactor centerline temperatures agreed well with the no-soot line. The departure from the line at high equivalence ratios was probably due to the larger amount of water formed at these ratios.

### Carbon-Atom Balance

The carbon-atom balance across the catalyst bed was calculated from the measured reaction products in table I. Changes in the number of moles of gas due to chemical reaction were accounted for by using nitrogen as a reference gas and balancing the carbon-nitrogen ratio of the fuel-air mixture entering the catalyst with the

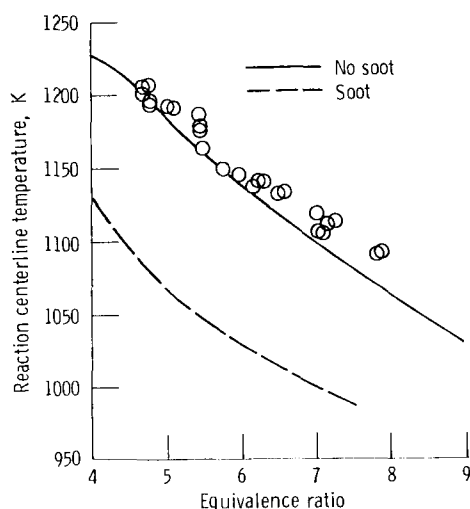


Figure 10.—Comparison of measured reaction temperatures with calculated equilibrium temperatures.

carbon-nitrogen ratio of the product gases. Plotting the percentage of initial carbon in the product gases as a function of the measured reaction temperature (fig. 11) showed that all reactant carbon can be accounted for by gas-phase species in the product stream. The departure from the 100 percent line at the lower temperatures may be due to the loss of the less volatile products in the cold trap.

### Visual Observations of Product Gases

The reaction products were observed through opposing calcium fluoride windows located 7.6 cm downstream of the catalyst bed. Although the gases were always completely transparent and showed none of the characteristic radiation associated with a sooting flame, a faint yellow-orange light was observed in the reactor. A closer inspection of the inside of the reactor indicated that the light was reflecting off the inside of the port leading to the opposite window. This suggested that the source of the light was the catalyst bed itself and not the gas. The radiation emitted by a black body source at 1150 K was

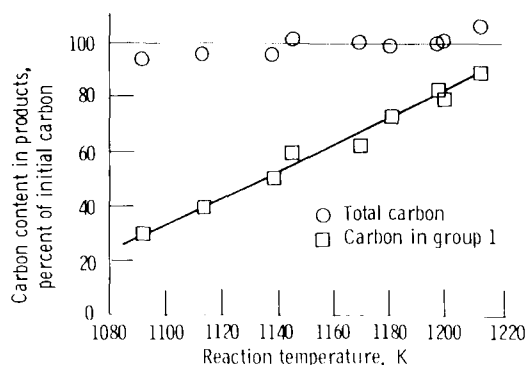


Figure 11.—Carbon atom balance and percentage of carbon found in molecules having two or fewer carbon atoms.

viewed to see how bright black body radiation is to the human eye. It was clear that if hot carbon were present in the gas phase, there would be observable amounts of light in the gas regardless of any catalyst glow.

### Hydrogen-Carbon Ratio

It was anticipated that oxygen-containing organic compounds would be formed by the partial oxidation process. However, at the test conditions used in these experiments, gas-phase reactions were so rapid that the reaction continued beyond this stage. The gas analysis consistently showed that the reactions involving oxygen always formed carbon monoxide, carbon dioxide, and water. Since both carbon monoxide and carbon dioxide are unable to form soot in hydrocarbon flames, they are excellent compounds with which to remove carbon atoms from the soot-forming process. The effective hydrogen-carbon ratio of the processed fuel was calculated by subtracting the amount of carbon in these two compounds from the total carbon in the product gases and dividing the remaining carbon into the initial hydrogen. This assumes that the water formed in the preburner was a source of hydrogen in the second-stage combustion process. Justification for this assumption comes from the work reported in references 9 and 10. Naegeli and Moses (ref. 9) found that water played an important chemical role in the reduction of soot in a T-63 combustor rig, and they suggest that it was probably a source of hydrogen. Mueller-Dethlefs and Schlader (ref. 10) show that water vapor did not behave as an inert diluent in a sooting flame but reacted chemically with the products and inhibited carbon formation.

At the highest reaction temperature the calculated hydrogen-carbon ratio for the products of the preburner (fig. 12) increased by more than 60 percent. Such an increase could convert a poor fuel into an excellent one.

### Other Features of Process

In addition to producing a soot-free gas and increasing the ratio of hydrogen to carbon, the products of this catalytic partial oxidation process had other favorable features: the high temperature resulting from the combustion process, and the large fraction of small molecules in the products. The temperature (1200 K) effectively broadened the flammability limit of the fuel and produced a very reactive hydrocarbon species. The burning rate of this species is extremely high, and reaction should take place as soon as air is added in the second stage of combustion. As a technique for fuel vaporization fuel-rich catalytic oxidation is superior to most heat exchanger techniques. The 1200 K outlet temperature well exceeds the 780 K fuel temperature obtained by Szetela (ref. 11), who studied the vaporization of Jet A. Fuel deposits and corrosion-erosion of the

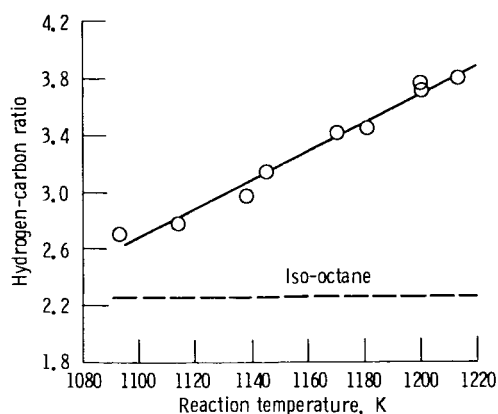


Figure 12.—Calculated hydrogen-carbon ratio for products of catalytic oxidation of iso-octane.

Although soot was not measured directly, three pieces of experimental data suggested that it was absent: (1) measured reaction temperatures followed closely those calculated for equilibrium with no soot formed, (2) the product gases were completely transparent and emitted none of the radiation characteristic of soot, and (3) a good carbon atom balance across the reactor was calculated from the product gases.

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tube walls limited the maximum usable temperature in these experiments. This property would be very useful in areas where the total dwell time is limited to a few milliseconds.

The products of fuel-rich catalytic oxidation contained mostly  $C_1$  and  $C_2$  compounds. At 1200 K over 80 percent of the carbon was in the small group 1 carbon molecules (fig. 11). The advantage of reducing large molecules to small ones can be seen in the work of Takahashi and Glassman (ref. 12). They demonstrate that the sooting tendency of a fuel in a premixed flame is related to the number of C-C bonds in the molecule. The larger the number of bonds, the greater the tendency to form soot. Thus the fuel-processing character of the preburner has produced a new fuel with much less of a tendency to form soot than the original fuel.

## Conclusions

Very fuel-rich catalytic combustion appears to be a viable approach to reducing the amount of soot formed in a practical combustion system. This first stage of a proposed two-stage combustion system operated soot free in the temperature range 1100 to 1200 K. The products of the catalytic oxidation of iso-octane at equivalence ratios of 4.8 to 7.8 showed a 20 to 68 percent increase in the effective hydrogen-carbon ratio and had over 80 percent of the initial carbon in molecules with two or fewer carbon atoms. These experiments demonstrated that changing the hydrogen-carbon ratio of a fuel does not necessarily require the addition of hydrogen. It can be accomplished by the removal of carbon atoms from the soot-forming process.

## References

1. Clayton, R.M.: A Partial Oxidation Staging Concept for Gas Turbines Using Broadened Specification Fuels. ASME Paper 79-GT-169, Mar. 1979.
2. Izquierdo, A.J.; and Hoult, D.P.: Methanol as a Soot Reducer in a Turbulent Swirling Burner. ASME Paper 84-JPGC-GT-2, Oct. 1984.
3. Street, J.C.; and Thomas, A.: Carbon Formation in Pre-mixed Flames. *Fuel*, vol. 34, no. 1, Jan. 1955, pp.4-36.
4. Clarke, A.E.; Hunter, T.G.; and Garner, F.H.: Tendency to Smoke of Organic Substances on Burning. *J. Inst. Petrol.*, vol. 32, no. 274, Oct. 1946, pp. 627-642; no. 275, Nov. 1946, pp. 643-655.
5. Burgoyne, J.H.; and Neale, R.F.: Limits of Inflammability and Spontaneous Ignition of Some Organic Combustibles in Air. *Fuel*, vol. 32, no. 1, Jan. 1953, pp. 17-27.
6. Graham, S.C.; Homer, J.B.; and Rosenfeld, J.L.J.: The Formation and Coagulation of Soot Aerosols. *Modern Developments in Shock Tube Research*, G. Kamimoto, ed., Shock Tube Research Society, Kyoto, Japan, 1975, pp. 621-631.
7. Tacina, R.R.: Experimental Evaluation of Fuel Preparation Systems for an Automotive Gas Turbine Catalytic Combustor. NASA TM-78856, 1977.
8. Gordon, S.; and McBride, B.J.: Computer Program for Calculation of Complex Chemical Equilibrium Compositions, Rocket Performance, Incident and Reflected Shocks, and Chapman-Jouquet Detonations. NASA SP-273, 1976.
9. Naegeli, D.W.; and Moses, C.A.: Effects of Fuel Properties on Soot Formation in Turbine Combustion. SAE Paper 781026, Nov. 1978.
10. Mueller-Dethlefs, K.; and Schlader, A.F.: The Effect of Steam on Flame Temperature, Burning Velocity and Carbon Formation in Hydrocarbon Flames. *Combust. Flame*, vol. 27, no. 2, Oct. 1976, pp. 205-215.
11. Szetela, E.J.; and TeVelde, J.A.: External Fuel Vaporization Study. (UTRC/R81-915326-15, United Technologies Research Center; NASA Contract NAS 3-21971.) NASA CR-165513, 1981.
12. Takahashi, F.; and Glassman, I.: Interpretation of Sooting Correlations Under Premixed Conditions. *Chemical and Physical Process in Combustion*, 1983, Combustion Research Institute, 1983, Paper 57.
13. Hunt, Russell A., Jr.: Relation of Smoke Point to Molecular Structure. *J. Ind. Eng. Chem.*, vol. 45, no. 3, Mar. 1953, pp. 602-606.

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16. Abstract  An experimental program on the catalytic oxidation of iso-octane demonstrated the feasibility of the two-stage combustion system for reducing particulate emissions. With a fuel-rich ( $\phi = 4.8$ to 7.8) catalytic combustion preburner as the first stage the combustion process was soot free at reactor outlet temperatures of 1200 K or less. Although soot was not measured directly, its absence was indicated. Reaction products collected at two positions downstream of the catalyst bed were analyzed on a gas chromatograph. Comparison of these products indicated that pyrolysis of the larger molecules continued along the drift tube and that benzene formation was a gas-phase reaction. The effective hydrogen-carbon ratio calculated from the reaction products increased by 20 to 68 percent over the range of equivalence ratios tested. The catalytic partial oxidation process also yielded a large number of smaller carbon-containing molecules. The fraction of fuel carbon in compounds having two or fewer carbon atoms ranged from 30 percent at 1100 K to 80 percent at 1200 K.					
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